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Description

**"Self-adhesive protective film with olefin rubber adhesive"**

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*proC!*  
The invention relates to a self-adhesive protective film for protecting the fresh paint finish of vehicles such as cars and for protecting freshly painted vehicle components against soiling and damage during assembly, transportation and storage, and to its use on vehicles, especially on cars.

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The preservation and protection of motor vehicles in the course of transportation from manufacturer to dealer has long been common practice.

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It is known that, in order to preserve cars, paraffin waxes are applied in a thickness of from 5 to 20  $\mu\text{m}$ . However, it has been found that, especially on horizontal areas of the vehicles, a thin and usually non-uniform layer of this nature does not afford adequate protection against external influences such as, for example, the corrosive action of bird droppings.

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A considerable disadvantage of sealing with paraffin wax is the need to remove the preservative using a steam jet, surfactants or solvents. Environmentally sound recovery and disposal of the residues are the cause of great complexity in terms of apparatus, and of very high costs to boot.

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(Self-adhesive surface protective films for motor vehicles have also been known for some time. In the majority of cases these are permanently adhesive films for protection and decoration, such as an anti-stonechip film, for example. These self-adhesive films remain permanently on the vehicle following their application.)

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(Reversibly adhering self-adhesive films for protecting the car during transportation have so far been used only in a few isolated cases and without great success.) The object of the invention was to remedy this situation and, in particular, to provide a self-adhesive protective film which does not have the disadvantages of the prior art, or at least not to the same extent. This object is achieved by a self-adhesive protective film as characterized in more detail in the patent claims.

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### Description of the invention

5 The adhesive film of the invention is a protective film for use on painted vehicles, especially cars, in particular having an adhesive comprising an essentially amorphous copolymer of at least two different  $\alpha$ -olefin monomers with a number of in each case from 2 to 12 carbon atoms and at least one diene as comonomer, where no  $\alpha$ -olefin should have a proportion of 75 mol% or more, and having a bond strength of from 0.2 to 10 2.8 N/cm, preferably from 0.3 to 1.5 N/cm on steel (AFERA Method 4001, corresponding to DIN EN 1939). The number of carbon atoms of the  $\alpha$ -olefins is between 2 and 12. Examples are linear alkenes, such as ethylene, propene, 1-butene, 1-hexene and 1-octene, and isoalkenes, such as 3-methyl-1-butene or 4-methyl-1-pentene. Suitable dienes are those 15 common for the preparation of EPDM rubber, examples being 1,4-hexadiene, dicyclopentadiene or, in particular, 5-ethylidene-2-norbornene (ENB). The proportion of diene in the polymer is preferably between 0.5 and 10% by weight. The proportion of the further comonomers (third and any other comonomers) should in particular be below 30 mol% if they are 20 non-olefinic comonomers. The latter comonomers may be polar, such as vinyl acetate, esters of acrylic or methacrylic acid, vinyl chloride, vinyl ethers or acrylonitrile, or apolar, such as isobutene, styrene or  $\alpha$ -olefin.

25 The Mooney viscosity ML (1+4) 125°C should be below 50, preferably below 30, so that the viscosity of the melt or solution is not too high. It is tested in accordance with ASTM D 1646.

It is advantageous to crosslink the adhesive composition. This increases the thermal stability (under alternating climatic conditions, for example); 30 peel increase on rough substrates or apolar substrates, such as olefin rubber window seals, is reduced. For crosslinking, suitable crosslinking agents are those customary for EPDM rubber. Preference is given to the technique of radiation crosslinking, especially with UV radiation and electron beams. In the case of UV radiation, the adhesive composition is 35 irradiated from the adhesive side. For the use of photoinitiators or the addition of crosslinking promoters such as esters of allyl alcohol, of methacrylic or of acrylic acid to the adhesive composition it is possible to reduce the radiation dose.

To high a proportion of polar non-olefinic monomers, however, increases the sticking force to the painted metal vehicle panel following storage under alternating climatic conditions. It is therefore advantageous to keep the proportion of polar comonomers below 20 mol% and, in particular, to omit them entirely; in this case, then, the copolymer comprises at least three apolar monomers.

The proportion of each of the  $\alpha$ -olefinic monomers should be below 75 mol%; more favourable is a proportion of not more than 65 mol%. The most suitable are terpolymers comprising three  $\alpha$ -olefins, whose proportion of  $\alpha$ -olefinic monomers is in each case between 5 and 60 mol%. (Limiting the proportion of individual monomers avoids increased sticking forces following storage under alternating climatic conditions, avoids poor tack on application, and avoids deformation of the paintwork.) Deformations comprise visually perceptible and irreversible changes to the painted surface, which result when the fresh, not yet fully cured paint has been covered with an inappropriate protective film.

In order to optimize its properties, especially its adhesion to specific paints, the self-adhesive composition employed can be blended with one or more additives, such as tackifiers (resins), plasticizers, fillers, pigments, UV absorbers, light stabilizers, anti-ageing agents, crosslinking agents, crosslinking promoters or elastomers.

Examples of such elastomers are EPM rubber, polyisobutylene, butyl rubber, hydrogenated block copolymers of styrene and dienes, or acrylate copolymers. Examples of suitable tackifiers are hydrocarbon resins (comprising unsaturated C5 or C7 monomers, for example), terpene-phenolic resins, terpene resins made from raw materials such as  $\alpha$ - or  $\beta$ -pinene, aromatic resins, such as indene-coumarone resins, or resins of styrene or  $\alpha$ -methylstyrene, such as rosin and its derivatives, such as disproportionated, dimerized or esterified resins, it being possible to employ glycols, glycerol or pentaerythritol, and also others as listed in Ullmanns Enzyklopädie der technischen Chemie, Volume 12, pp. 525-555 (4th ed.), Weinheim. Resins which are stable to ageing and have no olefinic double bond are particularly suitable, examples being hydrogenated resins.

Suitable fillers and pigments are, for example, carbon black, titanium dioxide, calcium carbonate, zinc carbonate, zinc oxide, silicates or silica.

- 5     Suitable UV absorbers, light stabilizers and anti-ageing agents for the adhesive compositions are the same as those listed below for the stabilization of the film.

- 10     Examples of suitable plasticizers are aliphatic, cycloaliphatic and aromatic mineral oils, diesters or polyesters of phthalic acid, trimellitic acid or adipic acid, liquid rubbers (e.g. nitrile rubbers or polyisoprene rubbers), liquid polymers of butene and/or isobutene, acrylates, polyvinyl ethers, liquid resins and soft resins based on the raw materials for tackifier resins, wool wax and other waxes, or liquid silicones. Plasticizers which are stable to  
15     ageing and have no olefinic double bond are particularly suitable.

- 20     Crosslinking agents are, for example, phenolic resins or halogenated phenolic resins, melamine resins and formaldehyde resins. Examples of suitable crosslinking promoters are maleimides, allyl esters, such as triallyl cyanurate, and polyfunctional esters of acrylic and methacrylic acid.

- 25     For some paint systems it is advantageous to add constituents of the paints to the adhesive in order to reduce the migration of paint constituents (such as fatty acid esters) from the paint into the adhesive composition. Paint constituents of this kind are described in more detail in EP 0 763 584 and US 5,612,135.

- 30     It is advantageous, moreover, for recycling and energy recovery if the adhesive and, in particular, the entire protective film is free from halogen.

- 35     (The backing used for the adhesive comprises thermoplastic films, preferably polyolefin films.) These may consist, for example, of polyethylene, polypropylene and their mixtures or copolymers (e.g. random copolymers). Appropriate thicknesses for the backing films are from 20 to 80  $\mu\text{m}$  (including, if appropriate, the adhesion promoter layer). The softness of the backing film is relevant to the flexibility of the protective film during application; the force at 10% extension should not exceed 25 N/15 mm, preferably 16 N/15 mm, either in the lengthwise or transverse

direction. On account of their stability to shrinkage under hot conditions and their good flexibility, propylene copolymers are particularly suitable. For improving the adhesion between film and adhesive it is advantageous, although not absolutely necessary, to use an adhesion promoter layer; in  
5 that case the backing film consists of the base layer and the adhesion promoter layer. The latter consists preferably of polymers formed from predominantly olefinic monomers and/or components of base layer and/or adhesive. With particular preference the adhesion promoter comprises at least one polymer of which at least 50 mol% consists of one or more  
10  $\alpha$ -olefins. Examples of such polymers are thermoplastic EPM or EPDM elastomers, ionomers based on ethylene-(meth)acrylic acid copolymer, or maleic anhydride-modified polyolefins.

In order to provide the backing film with weathering stability it is sensible -  
15 and, in the case of polyolefins, generally vital - to add light stabilizers. In the context of application to the protective film, their function is primarily to avoid embrittlement of the backing film. In the case of a multilayer backing film the protection relates in particular to the base layer. Light stabilizers of this kind are described in Gaechter and Müller, Taschenbuch der  
20 Kunststoff-Additive [Pocket Book of Plastics Additives], Munich 1979, in Kirk-Othmer (3rd) 23, 615-627, in Encycl. Polym. Sci. Technol. 14, 125-148 and in Ullmann (4th) 8, 21; 15, 529, 676. Hindered amine light stabilizers (HALS) in particular, such as CAS Nos. 106990-43-6, 65447-77-0, 70624-18-9 or 52829-07-9, are appropriate for the protective film of the  
25 invention. The amount of light stabilizer should be at least 0.15, preferably at least 0.30, % by weight, based on the backing film. The use of antioxidants for the film (e.g. Irganox 1010, or trisnonylphenyl phosphite) is advantageous but not absolutely necessary. Further suitable UV absorbers, light stabilizers and anti-ageing agents are listed in  
30 EP 0 763 584 on page 5.

The light stabilizers referred to for the film can also be employed for the adhesive composition. Such an addition raises the ageing stability of the adhesive composition, especially under UV exposure of more than 100 kLy  
35 (kilolangleys), but is generally unnecessary for applications entailing less than 6 months of outdoor weathering. In the case of the polyisobutylene homopolymer adhesives or butyl rubber adhesives which are not in

accordance with the invention, such an addition is vital to prevent residues of adhesive under very severe UV exposure.

5 The light stability of backing film and adhesive can also be improved by other additives in the protective film, especially in the base layer of the backing film. Such an improvement can be brought about by UV absorbers (e.g. Tinuvin P, Ciba) or, primarily, by means of reflective pigments (e.g. titanium dioxide). The protective film of the invention is intended as a high-grade branded product and therefore has a permeability for UV radiation in  
10 the range from 290 to 360 nm of less than 1%, preferably of less than 0.1%.

15 The adhesion promoter can be applied by coextrusion with the base film or by coextrusion with base film and adhesive, or by coating onto the base film.

One advantageous embodiment is to (apply the adhesion promoter simultaneously with the extrusion of the film, so that the resulting coextruded film need only be coated with adhesive.) The optimum technical  
20 solution for the protective film of the invention is the simultaneous coextrusion of film and adhesive (including, if appropriate, an adhesion promoter layer).

25 The particular significance of this invention, although residing inter alia in the process for preparing the protective film and in the composition of the backing film, consists primarily in the composition of the pressure-sensitive adhesive layer of the invention and in the combination of these factors.

#### Prior art relating to car protection films

30 When tested by applying them to painted metal panels and storing these panels under alternating climatic conditions, known apolar uncrosslinked self-adhesive compositions show better paint compatibility than polar compositions. By paint compatibility is meant absence of paint film  
35 deformation and ease of peel following storage under alternating climatic conditions. On the other hand, however, such compositions are too soft (insufficiently cohesive) and show residues of composition when the film is peeled off. If, therefore, such compositions are crosslinked by chemical or

- radiative means, they lead to unwanted paint film deformation. An exception is formed by self-adhesive compositions based on natural rubber resin, which can be peeled off again without residue and with only minor paint film deformation. However, these compositions are not stable to ageing on exposure to UV radiation. This leads to severe, greasy or hard paintlike residues on the coated metal panel following extreme stresses over a prolonged period (from three to six months) as occur, for example, in Florida.
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- 10 Also known are polyacrylate compositions. If uncrosslinked polyacrylate compositions are subjected to storage under alternating climatic conditions they exhibit good compatibility with paint surfaces. On the other hand, however, they are of such little cohesion that when the film is peeled off they leave residues of the adhesive composition on the substrate. If these
- 15 compositions are strongly crosslinked chemically or by radiation, they can be peeled off without residue but, on the other hand, cause permanent deformations on the paint surface and in some cases, moreover, show inadequate adhesion when bonded to curved painted areas.
- 20 Japanese Patent Application JP 02 199 184 discloses a radiation-crosslinkable pressure-sensitive adhesive which for protective use on paint films must be formulated with a low glass transition temperature in order to prevent permanent deformations of the paint film. In this case there are problems owing to the inadequate adhesiveness of the self-adhesive film
- 25 on the vehicles during application and transportation.

This also applies to acrylates as described in US 5,612,136. The process of irradiation disclosed therein, moreover, damages the film, thus reducing its weathering stability, if irradiation is carried out for so long that the residual monomers are fully removed by polymerization. At lower doses of irradiation, the content of residual monomers is so high that they migrate into the vehicle finish and thereby cause it to swell. A further disadvantage is the migration of photoinitiators into the paint, where they reduce its UV stability.

35 European Patent Application EP 0 519 278 discloses, for protecting cars, a film comprising a backing which is coated with a rubber-based pressure-sensitive adhesive, based especially on polyisobutylene, having a dynamic

modulus of elasticity of from  $2 \times 10^5$  to  $7 \times 10^6$  dyn/cm<sup>2</sup>, corresponding in SI units to a value of from  $2 \times 10^4$  to  $70 \times 10^4$  Pa, at 60°C. Performance tests conducted with a self-adhesive film of this kind indicate relatively good compatibility with paint surfaces. The adhesiveness following storage under alternating climatic conditions on paints common in the car industry, however, is so low that the bond strength required in practice is not always adequately attained. Especially under the influence of moisture on the film, the bond strength is frequently reduced to such an extent that the film becomes detached, during transportation, from the vehicle it is protecting, so that there is no longer any protective effect. Furthermore, the self-adhesive composition shows no compatibility with the sealing rubbers (sealing profiles) which are common in carmaking; when the protective film is peeled away from window profiles, residues of the adhesive coating composition remain on the rubber. When the protective film is peeled off, edges with residues of adhesive remain, which can be traced back to the breakdown of the adhesive under UV weathering.

JP 95-325285 describes a similar product. Polyisobutylene is again proposed as the adhesive composition, although it may include butyl rubber (polyisobutylene with double bonds).

European Patent Application EP 0 592 913 describes a surface protection film for the transportation of cars, which is composed of a copolymer of unsaturated, polar comonomers and  $\alpha$ -olefins, especially of EVAc. In the case of this protective film there is no application of an additional adhesive coating. A film of this kind, while admittedly of simple construction, nevertheless displays distinct disadvantages in terms of its use. The bond strength is very low; this defect can be remedied by heating in the course of application. In addition, unless these films are provided with a protective layer or a release covering, they lead to blocking, as taught by EP 0 768 356. A particularly serious consideration is that the films described show very severe paint film deformation and very great difficulty of removal following use.

The object, therefore, is to find an adhesive film which possesses sufficiently high initial bond strength that it can be bonded under tension (application of the adhesive film to curved areas) without becoming detached and yet following prolonged storage (up to one year under



weathering) can still easily be peeled off again. Accordingly, there has been no lack of attempts to remedy this deficiency. The EVAc adhesive film described in DE 195 32 220 is markedly superior to the product described in EP 0 592 913, but when peeled off after use still shows a bond strength which is too high to allow the adhesive film to be peeled off without tearing and without excessive effort by the user. With one-component paints, moreover, there is paint film deformation.

The increase in bond strength following outdoor storage, which the skilled worker calls peel increase, is caused by interactions - especially polar forces - of the adhesive with the paint. The skilled worker will therefore avoid polar comonomers such as acrylate or vinyl acetate. The polyisobutylene referred to in the abovementioned EP 0 519 278 is an adhesive which is appropriate in this context. The disadvantage, however, is the ageing behaviour. Polyisobutylenes are known to be soft (of low cohesion), especially following ageing as induced by heat or UV radiation. This leads to residues on the paint following removal. For this reason, in the case of the commercial adhesive film based on polyisobutylene, the films are highly pigmented - the destructive influence of light should be kept away from the adhesive as far as possible. In the edge region, however, the adhesive is exposed directly to UV light, leading to severe residues there. Attempts to avoid this are made by adding antioxidants and hindered amine light stabilizers (HALS) to the polyisobutylene; these additives are described in US 5,601 917.

Adhesives comprising hydrogenated styrene-diene block copolymers are substantially more stable to UV, and their use is described in the utility model DE 296 04 473 U1. A significant disadvantage of such block copolymers is their thermally reversible crosslinking via the styrene domains. If an adhesive film prepared from these polymers is peeled off in the summer from a vehicle which has become warm in the sun, the adhesive remains to a large extent adhering to the paintwork, since the cohesion of the adhesive compositions is less than that of the adhesion to the paintwork. Heating leads to shrinkage of the protective film and, as a result, the adhesive - which is soft under hot conditions - transfers smearingly onto the metal panel at the retreating edges of the adhesive film.

EP 0 661 364 describes a surface protection film comprising an adhesive composition which exhibits "strong initial tack" (p. 2, line 6) and is therefore inappropriate for the purposes of the present invention; pages 3 and 6 describe bond strengths to steel of up to 1 kg/25 mm, corresponding approximately to AFERA sticking forces to steel of up to 4.0 N/cm. To limit the peel increase behaviour on exterior weathering and/or storage under alternating climatic conditions it is important to restrict the proportion of polar comonomers as a whole and to limit the proportion of each individual  $\alpha$ -olefin monomer, something which is not undertaken by the cited invention. The films described, moreover, are not light stable, since no measures are taken - such as the addition of HALS or light-reflective pigments - to achieve the light stabilization necessary for this utility. The use of protective film on the outside of vehicles exerts particularly stringent requirements in terms of light stability, especially in the UV range, so that for this reason too protective films of this kind are completely unsuited to this utility. On application to vehicles an important part is played, owing to curved areas, by the extensibility of the film: the cited invention, however, emphasizes the suitability for planar areas ("plates" and "boards") and therefore does not attempt to limit the force at 10% extension.

WO 96/37568 describes the use of polyhexene and/or polyoctene for an apolar pressure-sensitive adhesive. The polymers described in the examples exhibit little peel increase but owing to their low cohesion, caused by the low molecular weight of customary commercial polymers of this kind, these polymers likewise lead to residues, which it is attempted to avoid by adding other polymers, referred to therein as cold flow restricting agents. For practical purposes, nevertheless, these adhesives are of inadequate cohesion (are too soft), which leads to residues after weathering, especially if the adhesive tape shrinks on exposure to heat.

#### Properties of the protective film of the invention

For the skilled worker it was surprising and unforeseeable that an adhesive composition which consists essentially of a copolymer of at least three monomers, including at least two  $\alpha$ -olefins having in each case from 2 to 12 carbon atoms and a proportion of in each case less than 75 mol%, and at least one diene, would have the desired combination of properties:

- low peel increase
  - good UV resistance
  - no paint film deformation
  - sufficient bond strength on application to curved surfaces
- 5    - high cohesion (no residues on peeling or on shrinkage of the protective film).

The very high weathering stability (resistance to UV light), in particular, is a completely surprising property.

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On the one hand, these self-adhesive compositions feature good strength of adhesion to a variety of coating materials common in the automotive industry, even under the effect of moisture or humidity, with the result that the protective film does not become detached from the vehicle even under  
15    the effect of wind or under tension due to bonding to curved surfaces. Furthermore, the self-adhesive composition exhibits a sufficient bond strength within the first few minutes following application, so that after just half an hour, for example, the protective film can be exposed to a fast airstream (up to 160 km/h) and yet, on the other hand, is not difficult to  
20    remove following prolonged use. In addition, the self-adhesive composition of the invention ensures a very low unrolling force. In particular, on a 65  $\mu\text{m}$  thick film consisting predominantly of EP copolymer, the self-adhesive composition of the invention shows no paint film deformation on metal panels which have been coated with polyurethane and heat-treated at  
25    130°C for 30 minutes and following storage under alternating climatic conditions as detailed in Example 1 of this description.

The peel force of the protective film of the invention from two-component PU coating materials is greater than 0.1 N/cm when fresh and below  
30    3 N/cm following storage under alternating climatic conditions (in accordance with AFERA Method 4001). In addition, irradiation of the protective film with UV light, for example with Xenotest 1200 at 55°C for 3000 hours, leads to no impairment to the properties of this protective film. There is no embrittlement of the film, and neither does the self-adhesive  
35    composition cause paint film deformation or discoloration and nor do residues of composition occur when the protective film is removed.

The protective film of the invention is therefore particularly suitable for protecting the fresh paint finish of cars during assembly or transportation, or as a protection for freshly painted steel panels during machining and transportation. In this context the protective film can be bonded just half an  
5 hour after the coated surfaces have passed through the oven, without any disadvantages whatsoever, despite the fact that at this point in time the paint has still not yet fully cured. In addition, the protective film exhibits outstanding properties when used as edge-fastening tape for the additional fastening of self-adhesive masking films of large surface area.

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A further feature of the protective film of the invention is that it can be applied in a large width over the bonnet, roof and boot of cars and, owing to its flexibility, conforms very well to planar and even gently curved surfaces. It is thereby possible to protect the horizontal surfaces which are  
15 most at risk from soiling. However, even narrow areas such as, for example, the projection of the door below the windows, or bumpers, can easily be covered over. Protection of the vertical surfaces on the vehicle is particularly appropriate during its assembly.

20 The protective film is resistant to sunlight, moisture, heat and cold, with weathering stability of at least six months. The addition of titanium dioxide and of light stabilizers, in particular, leads to an improvement in the UV resistance of the protective film. Even very high sun levels as are encountered, for example, in Florida, do not cause the protective film to fail  
25 or detach, at least within a period of six months.

After application of the protective film and following storage for 14 days at alternating temperatures and under the effect of weathering, the self-adhesive composition does not give rise to any deformation of the  
30 underlying paint film. In addition, the strength of the protective film in comparison to preservation with wax ensures flawless protection against soiling, such as bird droppings, and against damage to the entire vehicle by minor mechanical events.

35 Following use, the protective film can be removed without residue and without tearing the backing film, despite the good adhesiveness required. Even on the rubber seals used widely on cars there are no residues of adhesive following its removal. Especially if the protective film is free from

halogen, material recycling thereof or energy recovery therefrom is possible.

5 In the text which follows, the invention will be illustrated on the basis of examples which are not, however, intended to restrict the invention.

### Examples

#### Example 1

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A film is manufactured by flat-film extrusion in a width of 1450 mm. It consists of a 50  $\mu\text{m}$  thick base layer and 15  $\mu\text{m}$  thick adhesion promoter layer. The base layer consists of 60 parts by weight of PP homopolymer, 30 parts by weight of LLDPE, 10 parts by weight of titanium dioxide and 0.3  
15 part by weight of a HALS (Tinuvin 770). The adhesion promoter layer consists of a compound comprising 30 parts by weight of PP homopolymer, 20 parts by weight of LLDPE and 50% by weight of the polymer described below as adhesive.

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The film has the following physical properties:

Overall thickness of film with adhesion promoter	65 $\mu\text{m}$	DIN 53370
Overall weight of film with adhesion promoter	63 $\text{g/m}^2$	DIN 53365
Tensile strength, lengthwise	30 $\text{N/mm}^2$	DIN 53455-7-5
Force at 10% extension, lengthwise	19 $\text{N/15 mm}$	DIN 53455-7-5
Tensile strength, transverse	20 $\text{N/mm}^2$	DIN 53455-7-5
Extension, lengthwise	450%	DIN 53455-7-5
Extension, transverse	450%	DIN 53455-7-5
Impact strength under tension, lengthwise	3000 $\text{mJ/mm}^2$	DIN 53448
Impact strength under tension, transverse	200 $\text{mJ/mm}^2$	DIN 53448

The adhesive prepared is a 10% strength solution of a copolymer consisting of 48% by weight each of propene and ethylene and 4% by weight of 5-ethylidene-2-norbornene, having a Mooney viscosity ML (1+4)

125°C of 28 in toluene, and it is applied to the film with a spreader bar and dried for four minutes at 80°C in a tunnel. The resulting protective film is trimmed at the edge and wound up into rolls 200 m long and 1400 mm wide. The thickness of adhesive is 20 µm. The Mooney viscosity  $M_L$  (1+8) at 125°C was measured as 35.

The self-adhesive film produced in this way can be unwound easily and without creases and when used to protect cars can be applied without problems. Owing to the good tack and ease of correction, the bonding processes can be accelerated. After use for up to a six-month period of bonding under outdoor weathering (the self-adhesive film can be peeled off again without defects.)

The protective film is characterized by the physical properties reproduced in the following table.

Overall thickness of protective film:	80 µm
Peel force from the two-component PU paint after 14 days of alternating climatic conditions (cycle 2 as indicated below) at a peel angle of 180° and a peel rate of 300 mm/min:	1.4 N/cm
Peel force from the reverse side at a peel angle of 180° and a peel rate of 300 mm/min:	0.1 N/cm
Bond strength on steel	0.3 N/cm
Bond strength on paint	0.3 N/cm

The alternating climatic conditions comprise the following cycles:

Cycle 1		Cycle 2	
Duration [h]	Temperature [°C]	Duration [d]	Temperature [°C]
4	80	3	90
4	-30	plus 4 times cycle 1	
16	40 at 100% relative humidity		

Cycle 2 is repeated a total of two times here.

The protective film was bonded to freshly painted metal panels (2-component PU paint) and peeled off after a week; no paint film deformation was in evidence. Samples bonded to paint were weathered at 97 kLy; following removal, no residues could be seen on the surface or in the edge region.

## 10 Example 2

A film was produced by the procedure of Example 1, with the base layer consisting of 80 parts by weight of a PP random copolymer with 5.5% of ethylene (Novolen 3300 MC, BASF), 10 parts by weight of LLDPE, 7 parts by weight of titanium dioxide and 0.45 part by weight of a HALS (Chimassorb 944, Ciba) and the adhesion promoter layer consisting of 20 parts by weight of the PP random copolymer and 80 parts by weight of LLDPE. This film was coated by the procedure of Example 1. The adhesive used is a polymer as in Example 1 but with addition of 5% by weight of Regalrez<sup>TM</sup> 116 (tackifier, Hercules), 10% by weight Levapren 700 (VA elastomer, Bayer), 0.5% by weight Irgacure 651 (Ciba), 1.5% by weight trimethylolpropane triacrylate, 0.2% by weight Irganox 1010 (Ciba) and 0.3% by weight Tinuvin 770 (Ciba). The thickness of adhesive applied is 16 µm. The protective film was crosslinked on the adhesive side under nitrogen using a UV lamp (medium-pressure Hg lamp, 120 W/cm) at a distance of 10 cm and at a speed of 10 m/min.

The film exhibit a force of 14 N/15 mm at 10% extension in the lengthwise direction. The bond strength to steel is 0.9 N/cm, to paint 0.9 N/cm (fresh) and 2.6 N/cm (following storage under alternating climatic conditions). The protective film was bonded to freshly painted metal panels (2-component

PU paint) and peeled off after a week; slight deformations of the paint are discernible in the edge region. Samples bonded to paint were weathered at 97 kLy; following removal, no residues could be seen on the surface or in the edge region.

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### Example 3

The protective film was produced by coextrusion of three layers including adhesive. The base layer consists of the raw materials described in  
10 Example 3. The adhesive was a polymer formed from 59% by weight ethylene, 37% by weight propene and 4% by weight 5-ethylidene-2-norbornene (granulated and powdered with amorphous silica), having a Mooney viscosity ML (1+4) 125°C of 22, with addition of 0.2% by weight of Irganox 1010 (Ciba) and 3% by weight Escorez 5000, liquid (plasticizer,  
15 Exxon).

The extruder for the base layer was charged with the raw materials set out in Example 2, that for the adhesive layer with the granulated powdered terpolymer, and the extruder for the in-between adhesion promoter layer  
20 with a mixture of 50 parts by weight of recycled protective film from Example 1 and 50 parts by weight of granulated adhesive from this example.

The bond strength of the resulting protective film on steel is 0.2 N/cm and  
25 on paint 0.2 N/cm (fresh) and 1.4 N/cm (following storage under alternating climatic conditions). The protective film was bonded to freshly painted metal panels (2-component PU paint) and peeled off after a week; no paint film deformation was in evidence.

Bonded metal panels of the same type were subjected to UV ageing  
30 (1750 h of Xenotest 150, corresponding to 97 kLy). Following the removal of the protective film no residues are in evidence, not even in the edge region. Samples bonded to paint were weathered at 97 kLy; following removal, no residues could be seen on the surface or in the edge region.

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#### Example 4

The protective film was produced as in Example 1 but with the following amendments: the adhesive composition consisted of 30% by weight of a terpolymer (56% by weight ethylene, 38.8% by weight propene and 5.2% by weight dicyclopentadiene, having a Mooney viscosity ML (1+4) 125°C of 43), 55% by weight of a terpolymer prepared with metallocene catalyst (51% by weight ethylene, 44% by weight propene and 5% by weight 5-ethylidene-2-norbornene, with Mooney viscosity ML (1+4) 125°C of 20), and with addition of 0.1% by weight each of Irganox 1070 and Chimassorb 944, 5% by weight of a terpene resin (Resin PC 1150, Yasuhara Chemical), 15% by weight of a liquid polybutene (Hyvis 5, BP Chemicals) and 2.5% by weight of triallyl cyanurate. The adhesive composition was crosslinked under nitrogen with electron beams (dose: 10 kGy).

The bond strength on steel is 0.8 N/cm, on paint 0.9 N/cm (fresh) and 2.2 N/cm (following storage under alternating climatic conditions). The protective film was bonded to freshly painted metal panels (2-component PU paint) and peeled off after a week; no paint film deformations are in evidence in the edge region. Samples bonded to paint were weathered at 97 kLy; following removal, no residues could be seen on the surface or in the edge region.

#### Comparative Examples

##### Comparative Example 1

Preparation is as in Example 1. The pressure-sensitive adhesive employed is a copolymer consisting of 80 mol% ethylene and 20 mol% 1-butene. The solvent used was hot toluene. The bond strength on paint is 0.2 N/cm (fresh) and 4.9 N/cm (following storage under alternating climatic conditions). The protective film tears when peeled off from the painted metal panel when pulling on one corner of an extensive bond. A protective film in accordance with this example exhibits severe paint film deformation.

## Comparative Example 2

As Comparative Example 1; the copolymer consists of 90 mol% ethylene and 10 mol% 1-butene. Hot toluene is necessary as the solvent. The bond strength on painted sheet metal and on steel is less than 0.1 N/cm.

## Comparative Example 3

As Example 1 but with a terpolymer of 80 mol% ethylene and 10 mol% each of propene and 1-butene. The bond strength on paint is 0.5 N/cm (fresh) and 4.2 N/cm (following storage under alternating climatic conditions). The protective film according to this example exhibits severe paint film deformation.

## Comparative Example 4

As Example 1, but with a copolymer of 70 mol% vinyl acetate and 30 mol% ethylene. The bond strength on steel is 1.0 N/cm, on paint 0.9 N/cm (fresh) and 3.6 N/cm (following storage under alternating climatic conditions). When bonded to fresh paint, severe deformations can be observed.

## Comparative Example 5

The preparation is as in Example 1, with the adhesive employed being a mixture of polyisobutylenes; 25 parts by weight have a molecular weight  $M_w$  of 1.2 million, 75 parts by weight an  $M_w$  of 35 thousand. The bond strength on paint is 0.6 N/cm (fresh) and 1.8 N/cm (following storage under alternating climatic conditions). Samples bonded to paint were weathered at 97 kLy; following their removal, only slight residues were to be seen on the surface but very severe residues in the edge region. When bonded to fresh paint, slight paint film deformations are in evidence in the edge region.